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RADIOACTIVITIES IN RETURNED LUNAR MATERIALS AND IN METEORITES

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Semiannual Progress Reports No. 6 & 7

For the period 1 August 1985 through 31 July 1986

Principal Investigator
Dr. Edward L. Fireman

August 1986

Prepared for
National Aeronautics and Space Administration
Johnson Space Center
Houston, Texas

Smithsonian Institution
Astrophysical Observatory
Cambridge, Massachusetts 02138

The Smithsonian Astrophysical Observatory
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The NASA Technical Officer for this grant is Dr. I. D. Browne, Code SN2, Lyndon B. Johnson Space Center, Houston, Texas 77058.

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During the past 12 months we carried out a preliminary carbon-14 study on lunar soil with the University of Toronto Iso Trace accelerator mass spectrometer (Attachment 1). This accelerator was recommended to us for our ^{14}C work by Dr. R. Schneider of A.S. and E., who was the field engineer during the assemblage and start-up operation of the accelerator. After our preliminary study using CO_2 from 10084,937 soil, which had previously been counted with low-level mini-proportional counters, it became clear to me that the Toronto accelerator could carry out $^{14}\text{C}/^{13}\text{C}/^{12}\text{C}$ ratio measurements on 1 gram meteorite and lunar samples and that the ^{14}C measurements are done with higher precision and better reliability than elsewhere. I instituted a collaborative program with the University of Toronto Iso Trace accelerator group, which I expect will be scientifically fruitful. Arrangements have been made for Dr. R.P. Beukens of the Toronto Accelerator Group to spend time in our laboratory-extracting the carbon compounds from Antarctic meteorite and lunar samples and converting the compounds to CO_2 .

During the past two years, we developed a uranium-series dating method for polar ice and are applying this method to ice from the Allan Hills site, Byrd core, and the Beardmore glacier. Our publications during the past 12 months (Attachments 2, 3, 4, 5 and 6) have been mainly in this area.

Attachments

1. Carbon-14 in Lunar Soil by Accelerator Mass Spectrometry, R.J. Schneider, E.L. Fireman, R.P. Beukens, and W.E. Kieser, submitted to Journal of Geophysical Research, April 25, 1986.
2. Uranium-Series Dates for Ice from Two Allan Hills Locations (abstract), E.L. Fireman, Lunar and Planetary Science XVII, Part 1, p. 226, 1986.

3. Uranium Series Dating of Allan Hills Ice, E. L. Fireman, Journal of Geophysical Research, Vol. 91, No. B4, p. D539, 1986.
4. Correction to "Uranium Series Dating of Allan Hills Ice," E. L. Fireman, Journal of Geophysical Research, Vol. 91, No. B8, p. 8393, 1986.
5. Uranium-Series Study of Ice near the Bottom of the Byrd Core, E. L. Fireman (abstract), submitted to the September 22 to 25, 1986 Meeting of the Meteoritical Society.
6. Uranium-Series Dating of Antarctic Ice, submitted to Antarctic Journal of the United States, May 1986.

ATTACHMENT 1

Carbon-14 in Lunar Soil by Accelerator Mass Spectrometry

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Abstract

The $^{14}\text{C}/^{12}\text{C}$ ratios in the carbon released from 1.00 g of lunar soil 10084.937 (74-125 μm grain size) at 400, 600, 800 and 1000°C were measured with the University of Toronto IsoTrace Laboratory's accelerator mass spectrometer. The $^{14}\text{C}/^{12}\text{C}$ ratios increased monotonically with increasing temperature from $(0.436 \pm 0.012) \times \text{modern}$ at 400°C to $(2.236 \pm 0.048) \times \text{modern}$ at 1000°C. The carbon released from lunar soil below 1300°C is thought to contain solar wind implanted carbon and no spallation carbon-14 produced by the action of cosmic rays. If this is true, then it is difficult to explain the $^{14}\text{C}/^{12}\text{C}$ ratio of $2.236 \times \text{modern}$ without invoking a $^{14}\text{C}/^{12}\text{C}$ abundance in the solar wind of at least 2.63×10^{-12} .

Introduction

The University of Toronto IsoTrace accelerator mass spectrometer facility [Beukins et al., 1986; Kieser et al., 1986] offers the possibility of high sensitivity $^{14}\text{C}/^{12}\text{C}$ ratio measurements on small ($\approx 1\text{ cm}^3$ STP) samples of CO_2 . This was used to analyze the carbon extracted from lunar soil. The carbon contents of lunar soils are large (100-300 ppm) compared to those in lunar rocks (5-10 ppm); furthermore, the extraction of carbon from lunar rocks requires above-melting temperatures ($> 1300^\circ\text{C}$) while extraction of carbon from lunar soils occurs at much lower temperatures. Chang et al. [1972, 1973], Gibson and Moore [1973], and Simoneit et al. [1973] showed that the carbon compounds in lunar soils are released principally between 500 and 1200°C and interpreted both the amounts and the temperature-release patterns as resulting from carbon implantation. Solar wind is the likely source of the excess carbon implanted in lunar soil. An important question can be addressed by accelerator mass spectrometry: What is the $^{14}\text{C}/^{12}\text{C}$ ratio in the recent solar wind implanted in lunar soil? In spite of considerable effort, the isotopic composition of the solar wind carbon is uncertain. Studies of carbon-14 extracted from surface lunar soils [Fireman, 1978], which indicated the presence of carbon-14 in recent solar wind, were limited by the sensitivity of the mini-proportional counters used. $^{13}\text{C}/^{12}\text{C}$ ratio studies [Becker, 1980; Norris et al., 1983] on the carbon extracted from lunar soils were uncertain because of possible terrestrial contamination. Lunar samples also contain spallogenic carbon-14 produced by the action of cosmic rays on the most abundant elements, principally oxygen. The spallogenic carbon-14 is difficult to extract by pyrolysis, requiring above-melting temperatures [Fireman,

1978]. The carbon-14 released below 1300°C must therefore be attributed to another source, either solar wind or contamination with terrestrial carbon.

A suite of CO₂ samples, which had been prepared by stepwise, 400, 600, 800, 1000°C temperature extractions from the 74 to 125 μm size particulates of lunar soil, 10084, were available. These CO₂ samples had been counted for carbon-14 with low-level proportional minicounters [Fireman, 1978]. We reanalyzed these samples with the IsoTrace accelerator mass spectrometer and compared the results.

Sample Preparation

The history of the CO₂ samples is as follows. A 1.00 g sample of lunar soil labeled 10084.937, which had been sieved into the 74 to 125 μm size range by King [1971], was received by Fireman [1978]. He placed the sample in a degassed molybdenum crucible and evacuated it overnight at room temperature. The temperature of the sample was raised by resistance heating and then held constant for 4 hours while the evolved gas was collected with an automatic Toepler pump. The temperatures used were 400, 600, 800, and 1000°C. The collected gas was passed over CuO at 650°C and the carbon compounds were converted to CO₂. The amounts of CO₂ obtained were 0.95 cm³ (STP) at 400°C, 0.60 cm³ (STP) at 600°C, 0.77 cm³ (STP) at 800°C, and 0.224 cm³ (STP) at 1000°C. After radon was removed from the CO₂, argon was added. The gas mixture was placed in a small proportional counter and counted for carbon-14. After several months of counting, the gas was removed from the counter and stored in glass bulbs.

During the past year, we decided to have these samples reanalyzed with the Toronto accelerator mass spectrometer. The gas was removed from the bulbs and the CO₂ separated from the argon by freezing the CO₂ in a cold trap at liquid N₂ temperature. The amounts of CO₂ recovered are given in

the second column of Table 1. These amounts were smaller than those commonly used in the IsoTrace sample preparation; therefore carrier "tank" CO_2 was added to increase the volumes to about 8 cm^3 (STP). The amounts of carrier CO_2 added to the samples are given in the third column of Table 1. This "tank" CO_2 had been counted for ^{14}C in a large volume counter, giving greater than 40×10^3 year age; and its $\delta^{13}\text{C}$ had been measured to be -43.3 per mil by conventional mass spectrometry.

The CO_2 samples were sealed in glass bulbs and taken to Toronto where they were converted to carbon targets by the following procedure. The CO_2 was reacted with lithium at 850°C to form lithium carbide. Distilled water was added to the lithium carbide to form acetylene, which was dried by freezing out the water vapor. The acetylene was then placed in a cracking cell where it was dissociated by a 1 kilovolt 60 Hz AC discharge and the carbon was deposited onto two aluminum electrodes. The carbon-coated electrodes were used for the accelerator ion source targets as 3 mm disks. Approximately 300 micrograms of carbon are deposited on each electrode in 12 minutes at acetylene pressures ranging from 11 to 5 torr. This quantity of carbon allows $^{14}\text{C}/^{12}\text{C}$ ratios to be determined with a 0.6% precision for modern terrestrial carbon in 1.5 hours.

Isotope Ratio Measurements

The targets were stored and transferred under vacuum and loaded into a target holder. One holder carried 3 lunar targets, one carrier gas target and two NBS Oxalic Acid I standards. Other target holders with duplicate targets were also used. A cesium ion beam of less than 1 mm in diameter sputtered negative carbon ions from the source target. The target moved in a programmed sequence so that the cesium beam sampled 16 different points on the target surface. From each target point, ^{12}C and ^{13}C ions were

selected for 0.5 seconds and accelerated to the 2.0 megavolt terminal, ^{14}C ions were then selected for 20 seconds, followed again by ^{12}C and ^{13}C ions for 0.5 seconds. The negative ions were stripped of several electrons at the terminal by passing through a gas stripping canal and accelerated further. Charge state +3. 8 MeV ions were selected by an electric analyzer. The ^{12}C and ^{13}C ions passed through one high energy spectrometer magnet into Faraday cups where their currents were measured. The ^{14}C ions passed through another high energy spectrometer magnet into a low-pressure gas filled ionization chamber, which has nearly 100% collection efficiency.

The carbon from the four lunar samples was measured twice (two targets) and the carbon from the carrier CO_2 was measured six times. The measured $^{13}\text{C}/^{12}\text{C}$ ratios represent the combined effect of natural, sample preparation and sputtering fractionation and the $^{14}\text{C}/^{12}\text{C}$ ratios were corrected for this fractionation to a base of $\delta^{13}\text{C} = -25$ per mil [Beukens et al., 1986]. The $^{14}\text{C}/^{12}\text{C}$ ratios were measured relative to the NBS Oxalic Acid I standard (1.175×10^{-12}) and were converted to absolute ratios using the absolute activity of this standard, determined by Karlén et al. [1964]. The averages of these measurements are given in Column 4 of Table 1; the errors are 1 σ errors. The fifth column gives the $^{14}\text{C}/^{12}\text{C}$ ratios of the samples (minus carrier) assuming a $\delta^{13}\text{C}$ of -43.3 per mil for the carrier and the sample. The last column gives the $^{14}\text{C}/^{12}\text{C}$ ratios of the samples (minus carrier) assuming a $\delta^{13}\text{C}$ of 0 for the samples and -43.3 per mil for the carrier. A comparison of the last two columns indicates that a large change in the $\delta^{13}\text{C}$ of the samples produces little change in the $^{14}\text{C}/^{12}\text{C}$ ratio.

Table 2 summarizes the results for the four temperature fractions, including the CO_2 released and the equivalent carbon weights. The fourth

column represents the measured $^{14}\text{C}/^{12}\text{C}$ ratios averaged over the last two columns of Table 1. The fifth column gives the ^{14}C activity of the soil in decays per minute per kilogram lunar soil (dpm/kg) as calculated from the released carbon, the measured $^{14}\text{C}/^{12}\text{C}$ ratios and the physical halflife of 5730 years. The errors represent only the 1σ errors due to the accelerator measurements (counting error on ^{14}C and errors in the ^{12}C and ^{13}C current measurements) and do not include the errors in the sample and carrier gas volumes. For a direct comparison, Fireman's [1978] values are given in the last column. His errors are the 1σ statistical counting errors for approximately 3 months of counting time. The comparison of the last two columns shows that the accuracy obtained in 2 hours of running time with the accelerator was 20 times better than obtained with 3 months of beta counting.

Results

As seen in the fourth column of Table 2, the $^{14}\text{C}/^{12}\text{C}$ ratios rise with increasing release temperatures, reaching 2.63×10^{-12} at 1000°C , which is 2.24 times the modern value. The $^{14}\text{C}/^{12}\text{C}$ ratios less than modern can be explained by a mixture of dead (zero carbon-14) solar wind implanted carbon with modern terrestrial carbon contamination in the soil 10084.937. The $^{14}\text{C}/^{12}\text{C}$ ratio of 2.24 times the modern value requires that the implanted solar wind carbon has at least the $^{14}\text{C}/^{12}\text{C}$ ratio of 2.63×10^{-12} .

The amount of carbon, 1.36 mg, obtained from 1.00 g of lunar soil 10084.937 is higher than expected, if lunar soils contain 300 ppm or less of carbon. It therefore appears that this soil sample is contaminated with terrestrial carbon. In stepwise temperature extractions, one would expect the release of the contamination carbon to decrease with increasing temperature. The fact that the $^{14}\text{C}/^{12}\text{C}$ ratios rise with increasing

temperatures indicates that the terrestrial contamination is mainly ancient (dead) carbon and the lunar carbon is active.

Fireman [1978] obtained significant ^{14}C activities in the 800°C and 1000°C temperature releases from the small grain size fractions ($\leq 37\mu\text{m}$) of lunar soil 10084. He attributed these activities to solar wind implanted ^{14}C . The last column of Table 2 shows that he did not observe ^{14}C activity in 74 to 125 μm grain size fraction of 10084 soil. Our results are consistent with his for the 400, 600°C results, slightly higher for the 800°C results and significantly higher for the 1000°C results.

In view of the scientific significance of solar wind with a $^{14}\text{C}/^{12}\text{C}$ of $\geq 2.63 \times 10^{-12}$ and also the high precision presently available with the Toronto accelerator mass spectrometer, a carbon isotopic composition versus release-temperature study for a complete set of grain-size fractions from a lunar surface and a subsurface soil sample should be undertaken.

Acknowledgements

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TABLE 1. $^{14}\text{C}/^{12}\text{C}$ Ratios in Stepwise Temperature Carbon Releases
from Lunar Soil 10084.937 (74-125 Micron Grain Size)

	Sample	Carrier	$(^{14}\text{C}/^{12}\text{C})$	$(^{14}\text{C}/^{12}\text{C})^*$	$(^{14}\text{C}/^{12}\text{C})^\dagger$
	Volume	Volume	with carrier	without carrier	without carrier
Sample	cm^3 (STP)	cm^3 (STP)	$(\times 10^{-14})$	$(\times 10^{-12})$	$(\times 10^{-12})$
Carrier CO_2	17.80		0.382 ± 0.031		
400°C	0.50	8.00	3.49 ± 0.09	0.512 ± 0.015	0.515 ± 0.015
600°C	0.52	8.00	3.83 ± 0.08	0.548 ± 0.013	0.551 ± 0.014
800°C	0.77	7.64	8.35 ± 0.14	0.842 ± 0.015	0.849 ± 0.015
1000°C	0.22	8.29	7.43 ± 0.15	2.627 ± 0.055	2.633 ± 0.055

* Normalized with $\delta^{13}\text{C} = -43.3$ per mil for the carrier CO_2 and sample CO_2 .

† Normalized with $\delta^{13}\text{C} = -43.3$ per mil for the carrier CO_2 and $\delta^{13}\text{C} = 0$ for the sample CO_2 .

TABLE 2. Total Carbon and $^{14}\text{C}/^{12}\text{C}$ Ratios in Stepwise Temperature Carbon Releases from 1 Gram of Lunar Soil 10084.937

Extraction Temperature (°C)	Released CO_2 cm^3 (STP)	Released Carbon (mg)	$^{14}\text{C}/^{12}\text{C}$ ($\times 10^{-12}$)	^{14}C Activity (dpm/kg)	Fireman [1978] ^{14}C Activity (dpm/kg)
400	0.95	0.51	0.513 ± 0.015	3.02 ± 0.09	2.2 ± 1.2
600	0.60	0.32	0.550 ± 0.014	2.04 ± 0.05	2.4 ± 1.2
800	0.77	0.41	0.845 ± 0.015	4.03 ± 0.07	1.5 ± 1.2
1000	0.224	0.12	2.630 ± 0.055	3.65 ± 0.08	-0.2 ± 1.2

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ATTACHMENT 2